Electron Correlations on a Mesoscopic Scale

Palstra, T.T.M.; Steigerwald, M.L.; Ramirez, A.P.; Kwon, Y.-U.; Stuczynski, S.M.; Schneemeyer, L.F.; Waszczak, J.V.; Zaanen, J.

Published in:
Physical Review Letters

DOI:
10.1103/PhysRevLett.71.1768

Publication date:
1993

Electron Correlations on a Mesoscopic Scale: Magnetic Properties of Transition Metal Telluride Cluster Compounds

T. T. M. Palstra, M. L. Steigerwald, A. P. Ramirez, Y.-U. Kwon, S. M. Stuczynski, L. F. Schneemeyer, J. V. Waszczak, and J. Zaanen

AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

(Received 22 December 1992)

We report the magnetic properties of a new class of materials: $Ni_9Te_6^{n+}$ and $Co_6Te_8^{n+}$ with $n=0,1,2$. These cluster compounds, which can be charged by chemical means from neutral to 2+, provide a unique and novel way to change the Fermi level. For most charge states we observe quenching of the spin and orbital moments at low temperatures, accompanied by a large value for the temperature independent susceptibility of the ground state. The generic presence of low-energy magnetic excitations in these compounds indicates that these systems exhibit strong electron correlations and form mesoscopic analogs of the mixed-valence–heavy-fermion compounds.

PACS numbers: 75.20.Hr, 36.40.+d

Traditionally, the study of materials has shown a dichotomy between the domain of chemistry, focusing on rather small molecular units, and that of solid state physics, dealing with macroscopic aggregates of atoms. Because of novel preparation techniques it has become possible to narrow this gap. In physics advanced lithographic techniques have resulted in novel structures in the area of mesoscopic physics. In chemistry new preparational approaches have yielded relatively large clusters of atoms, with properties different from the molecular and macroscopic scales [1].

The problem of strongly correlated electrons has been extensively studied in bulk systems. Recent work on the Kondo effect in quantum wires, however, has demonstrated that new phenomena emerge when such systems are reduced to mesoscopic size [2]. In general, little is known about physics at these length scales apart from localization studies, and the cluster analogs of itinerant magnets [3,4]. We approach this problem from the other side, namely, by building up from the atomic length scale, towards more complicated mesoscopic systems. For this purpose, we have synthesized a new class of cluster compounds: $Ni_9Te_6^{n+}$ and $Co_8Te_6^{n+}$ with $n=0,1,2$. These materials offer some unique properties: (1) The clusters are completely identical, order in a regular lattice, and large single crystals can be grown; (2) the passivating ligands form a weak bond to the cluster (different from, e.g., the metal-carbonyl clusters [4]); and (3) the clusters can be obtained in various charge states, without changing the structure significantly.

Our results indicate that the magnetic properties are unparalleled in either bulk or molecular magnetism [5,6]. The high-temperature moments are large and vary strongly with cluster and charge state, as is usual for small complexes containing d or f ions. However, we find as a generic feature that the effective moment is strongly reduced in the ground state. Moreover, we identify a large paramagnetic contribution to the low-temperature susceptibility, additionally indicating low lying magnetic excitations. At the same time, we expect that charge excitations are pushed to high energies, at least by finite size effects (the highest occupied molecular orbital–lowest unoccupied molecular orbital gap ~ 0.2 eV). We argue, following ideas by Fulde and co-workers [7], that these clusters form mesoscopic analogs of the mixed-valence–heavy-fermion materials.

In Fig. 1 we show the two cluster compounds under discussion. Each structure is completed by a passivating layer of neutral ligands of triethylphosphine (L). The ligands form a weak bond to the surface of the cluster and provide a gentle barrier between neighboring clusters. (These materials are electrically insulating.) Electrons can be chemically removed from the cluster sequentially; thus each salt $(Ni_9Te_6L_8)^{n+}(BF_4)^{n-}$ and $(Co_8Te_6L_6)^{n+}(BF_4)^{n-}$ with $n=0,1,2$ can be made as a pure solid. It was found that the structures change very little with electron count n.

We characterize the electronic state of the clusters by magnetization measurements, using a commercial SQUID magnetometer (Quantum Design). In Fig. 2 we show the effective magnetic moment p_{eff} (defined as $\sqrt{8\chi T}$) versus temperature T of all cluster compounds under discussion. This figure shows that the high-temperature effective moments per cluster are comparable to the value of a *single* metal ion. This indicates that the magnetic properties are related to the electronic structure of the cluster as a whole, and not to the magnetism of the individual atoms. At low temperature the moments decrease rapidly for four of the six compounds. It is difficult to obtain ground state moments from these measurements. Therefore, we have used another method to study the ground state properties.

In Fig. 3 we show the magnetization versus magnetic field at four temperatures: 2, 3, 5, and 10 K for the compound $Ni_9Te_6^{1+}$. The magnetization increases rapidly with magnetic field up to values of $\sim 1.5\mu_B$/cluster, but it never saturates even at the highest fields and lowest temperature. For a local moment system the magnetization should saturate when the magnetic field exceeds thermal energies, and is described by a Brillouin function. Thus,

0031-9007/93/71(11)/1768(4)$06.00

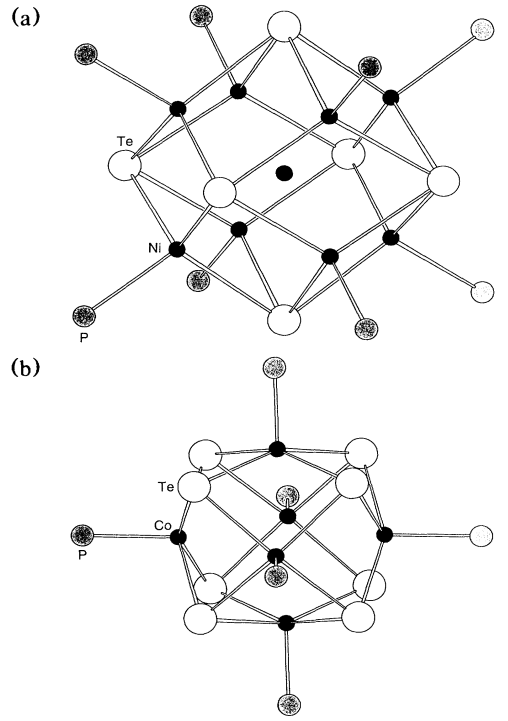

FIG. 1. (a) Crystallographically determined structure of $Ni_9Te_6(PEt_3)_8$. The large circles represent Te atoms, the small circles Ni atoms, and the intermediate-sized circles represent P atoms of the passivating ligands. The C and H atoms have been omitted for clarity. The average center-Ni surface-Ni distances are 2.47 Å. The average center-NiTe distance is 2.98 Å. The average surface-NiTe distance is 2.55 Å. Upon oxidation the cluster contracts slightly ($<1\%$). Complete structural details are given in Ref. [8]. (b) Crystallographically determined structure of $Co_6Te_8(PEt_3)_6$. The large circles represent Te atoms, the small circles Co atoms, and the intermediate-sized circles represent P atoms of the passivating ligands. The C and H atoms have been omitted for clarity. The average Co-Te distance is 2.52 Å. The average Co-Co distance is 3.23 Å. Upon oxidation the cluster contracts slightly ($<1\%$). Complete structural details are given in Ref. [9].

the susceptibility of the cluster has superimposed on the Curie behavior another contribution. The simplest model is to assume at low temperature a temperature independent susceptibility of Van Vleck type. We can separate these two terms by subtracting a constant value $\chi_{VV}H$ from the measured $M(H)$, and plotting the data as $M_{meas}-\chi_{VV}H$ versus B/T (magnetic field over temperature) [see Fig. 3(b)]. For the proper choice of χ_{VV}, the measurements nearly coalesce onto one line. The temperature dependent term fits the Brillouin function and yields a saturation moment M_{sat} of roughly $1\mu_B$. This shows that the magnetic ground state consists of a single spin-only electron per cluster and no interactions between the clusters. Turning now to the uncharged and the doubly charged Ni_9Te_6 clusters, a similar analysis shows that these clusters have a nonmagnetic ground state, exhibiting a small, noninteracting moment of only $0.15\mu_B$ and $0.32\mu_B$, respectively.

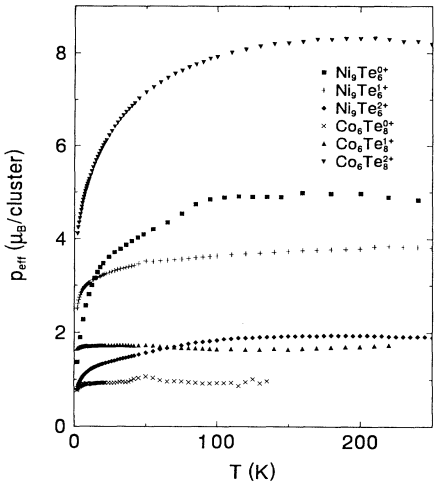

FIG. 2. Temperature dependence of the effective magnetic moment $p_{eff}=\sqrt{8\chi T}$ of $Ni_9Te_6^{n+}$ and $Co_6Te_8^{n+}$ with $n=0,1,2$ measured in a field of 0.1 T.

For the Co-Te cluster we find for the uncharged cluster a nonmagnetic ground state ($M_{sat}=0.02\mu_B$). The singly charged cluster has a ground state moment of $\sim 1\mu_B$. Finally, the doubly charged Co-Te cluster exhibits a magnetic moment of $\sim 2\mu_B$/cluster. We note that this ground state moment is reduced enormously from the effective moment at room temperature of $\sim 8\mu_B$. The low- and high-temperature moments are listed in Table I.

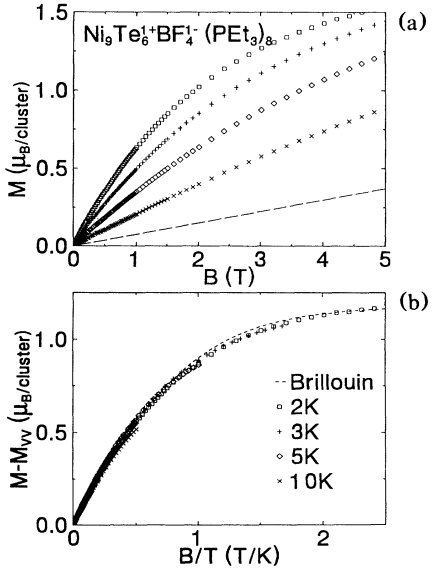

FIG. 3. Magnetic field dependence of the magnetization of $Ni_9Te_6^{1+}$ at 2, 3, 5, and 10 K. (a) shows the raw data. (b) shows the same data replotted as $M-\chi_{VV}H$ versus B/T, and compares the data with the theoretically expected Brillouin curve, using $M_{sat}=1.18\mu_B$/cluster.

TABLE I. Compilation of the magnetic data on the cluster compounds $Ni_9Te_6^{n+}$ and $Co_6Te_8^{n+}$: saturation moment M_{sat}, room temperature effective moment p_{eff}, temperature independent magnetic susceptibility χ_{VV}, derived from the low-temperature M versus H curves (see text), and the energy gap between the ground state and the excited state. cl denotes cluster.

Compound	M_{sat} (μ_B/cl)	P_{eff} (μ_B/cl)	χ_{VV} [(μ_B/cl)T]	Δ (K)
$Ni_9Te_6^{0+}$	0.15	4.9	0.14	20
$Ni_9Te_6^{1+}$	1.1	3.7	0.07	15
$Ni_9Te_6^{2+}$	0.32	1.9	0.07	15
$Co_6Te_8^{0+}$	0.02	0.9	−0.02	···
$Co_6Te_8^{1+}$	0.8	1.7	0.00	···
$Co_6Te_8^{2+}$	1.8	8.2	0.35	25

At the outset of the discussion we emphasize that the spins are delocalized over the whole cluster. A local moment picture involving $S=1$ Ni^{2+} and $S=\frac{1}{2}$ Ni^{1+} for $Ni_9Te_6^{n+}$, and $S=2$ Co^{3+} and $S=\frac{3}{2}$ Co^{2+} cannot account for the observed high-temperature moments. First, in a local moment picture the moments of both compounds should increase when removing electrons (the $3d$ orbitals are more than half filled), which is in disagreement with the data for $Ni_9Te_6^{n+}$ (see Table I). Second, the moment change in a local moment picture when removing one electron from a cluster is less than 5%, whereas, e.g., the moment change for $Co_8Te_6^{n+}$ is a factor of 4. Finally, the extended solid of Ni_9Te_6, bulk NiTe, has also delocalized orbitals and is a p-type semimetal [10]. Because of the low electronegativity of Te, the holes have a large amplitude on Te, tending to weaken the effects of interactions, and a rather conventional metal results. The formal charge of the Ni is 1.33+ for $Ni_9Te_6^{0+}$. We would expect that this mixed valence nature will further reduce the effect of magnetic interactions. Extrapolating these properties of the bulk to the clusters, we expect the clusters to be in the lowest spin state ($S=0$ or $\frac{1}{2}$) [11]. However, in striking contrast with the bulk compounds, the moments are large and one has to reconcile the large moments at room temperature with the low-spin ground states.

Now, having shown that the spins are delocalized over the cluster, we inspect molecular orbital scenarios to explain the strong variation of the high-temperature moments. Extended Hückel (tight-binding) calculations [12] for the undistorted O_h cluster $Ni_9Te_6^{0+}$ show orbitals of t_{2g}, t_{1g}, and e_g character in the immediate vicinity of E_F. These three orbitals are occupied by 12 electrons, isolated from other orbitals by relatively large ligand-field gaps, as shown in Fig. 4. Assuming that the Coulomb interactions are strongly screened by delocalization, the presence of these other orbitals can be neglected. It appears impossible to explain the variation of the high-temperature moments in terms of this set of orbitals. However, a strong uniaxial field (D_{4h}) splits the levels in

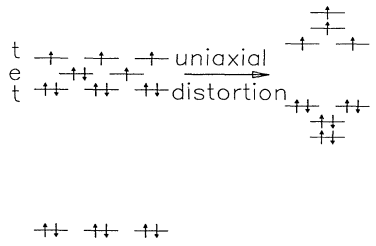

FIG. 4. Schematic representation of the orbital levels of $Ni_9Te_6^{0+}$ near the Fermi level as calculated by Wheeler [12]. A uniaxial distortion yields two groups of four orbitals split by the uniaxial field.

two groups of four orbitals (see Fig. 4). In the neutral cluster the upper group is half filled, explaining naturally the larger ($S=2$) spin, while the spin decreases if electrons are removed, as is observed. Molecular orbital calculations are not available for Co_6Te_8. However, regardless of the actual level structure, the dramatic change in spin state between $n=1$ and 2 cannot be accounted for.

Next, we address the temperature dependence of p_{eff} below 100 K. A temperature dependent moment is in fact more the rule than the exception in small d or f complexes [5,6]. This temperature dependence is caused by the small spin-orbit (SO) coupling in $3d$ systems. The unsaturated large temperature moments indicate that the ligand field splittings dominate, and the temperature dependence could therefore in principle be due to the SO coupling. However, this cannot be the case for $Ni_9Te_6^{0+}$ or $Co_6Te_8^{2+}$. In O_h symmetry the spin-only moment can be reduced at most by one unit ($J=S-1$), whereas experimentally we find a much larger reduction. Another explanation for the moment reduction is that these clusters undergo a conventional high-spin low-spin transition. However, these transitions are usually tied to a particular electron count (e.g., d^6 for $3d$ ions) and are accompanied by a strong coupling to the lattice. In these clusters, however, the quenching of the moment is a generic feature, unrelated to electron count and showing no relationship to the lattice. Therefore, we cannot explain the moment reduction in terms of either spin-orbit coupling or high-spin low-spin transitions.

The unconventional character of the magnetism in these clusters is further emphasized by the paramagnetic contribution to the low-temperature susceptibility, showing up in all cases where the moment is strongly temperature dependent. Such a contribution signals the mixing in by the magnetic field of excited terms into the ground state, and according to Van Vleck $\chi_{VV}=2\mu_B^2 T/\Delta$, with T the matrix element between the ground state and excited state, and Δ the energy difference. From a single ion perspective the Van Vleck susceptibility in the clusters appears to be anomalously large. For instance, asserting that Ni_9Te_6 is related to the $^1A_1$ low-spin ground state of d^6 the Van Vleck susceptibility would be given by $\chi=5.88/\Delta$, with Δ in kelvin [5]. In the low-spin Co-

compound hexamine [5] a gap of 30000 K yields $\chi_{VV} = 2\times10^{-4}$, in rough agreement with experiment. The χ_{VV} we observe in the cluster compounds are roughly 3 orders of magnitude higher, which means that the excitation energies are of the order of kelvins, in rough agreement with the energy scales suggested by the temperature dependence of the moments.

Summarizing our experiments, we find in these clusters a small energy scale governing the magnetic properties. The large high-temperature moments are quenched, accompanied by a large Van Vleck–like contribution at low temperatures. This kind of behavior seems to be rather general among the clusters studied here, occurring in four of the six compounds we have studied. It seems unlikely that this is due to an accidental near degeneracy of low-spin and high-spin terms. In fact, strong parallels exist with the magnetic phenomenology of heavy-fermion–mixed-valence metals [13]. Similar to our clusters, these materials are characterized by local moments ("Ni") immersed in a sea of weakly correlated conduction electrons ("Te"). The interaction between the local moments and conduction electrons leads to an energy scale for spin excitations which is exponentially smaller than single particle bandwidths, manifesting itself in the susceptibility as a crossover between free local moments at high temperatures and quenched moments at low temperatures. Moreover, a large paramagnetic susceptibility is found at low temperatures, which is now associated with the Pauli susceptibility, coming from quasiparticles whose (heavy) mass scale is set essentially by the spin dynamics. This physics already shows up in the case of a single magnetic ion in a normal metal, the Kondo problem [14]. Here, the local spin disappears at a characteristic temperature, the Kondo temperature T_K.

Recently, Fulde and co-workers suggested that similar effects might occur in molecular systems [7]. They pointed out that the scale for the spin dynamics is only indirectly related to the finite size splittings between the single particle states, and the splittings between spin states can be exponentially smaller than the finite size splittings, in the same way as the Kondo temperature is much smaller than a single particle bandwidth or exchange integral. In contrast to the ceranocene molecule considered by Fulde and co-workers, the telluride clusters cannot be reduced to an effective single impurity problem. It might be more appropriate to look at the telluride clusters as the mesoscopic equivalents of the heavy-fermion–mixed-valence systems. We note that in the cluster analogs of itinerant ferromagnets no indication is found for Kondo-like physics.

In conclusion, we have studied the cluster compounds $Ni_9Te_6^{n+}$ and $Co_6Te_8^{n+}$, with $n=0,1,2$. We observe moment reduction in the various charge states, accompanied by a large value for the temperature independent susceptibility in the ground state. This indicates a nonaccidental low-energy scale for magnetic excitations in these materials. These results are similar to the magnetic properties of mixed-valence–heavy-fermion materials. Further work is needed to characterize the magnetic excitation spectrum, and on other materials of the same type to see if these effects are as general as suggested by the present series of compounds.

[1] For a comprehensive review of recent work, see, e.g., *Proceedings of the Fifth International Meeting on Small Particles and Inorganic Clusters* [Z. Phys. D **19-20** (1991)].

[2] G. Chen and N. Giordano, Phys. Rev. Lett. **66**, 209 (1991); J. F. DiTusa, K. Lin, M. Park, M. S. Isaacson, and J. M. Parpia, Phys. Rev. Lett. **68**, 678 (1992).

[3] W. A. de Heer, P. Milani, and A. Chatelain, Phys. Rev. Lett. **65**, 488 (1990); J. P. Bucher, D. C. Douglas, and L. A. Bloomfield, Phys. Rev. Lett. **66**, 3052 (1992).

[4] L. J. de Jongh, J. Albino, O. de Aguiar, H. B. Brom, G. Longoni, J. M. van Ruitenbeek, G. Schmid, H. H. A. Smit, M. P. J. van Staveren, and R. C. Thiel, Z. Phys. D **12**, 445 (1989); B. J. Pronk, H. B. Brom, and L. J. de Jongh, Solid State Commun. **59**, 349 (1986); L. J. de Jongh, Physica (Amsterdam) **155B**, 289 (1989).

[5] J. S. Griffith, in *The Theory of Transition Metal Ions* (Cambridge, London, 1961).

[6] E. A. Boudreaux and L. N. Mulay, in *Theory and Applications of Molecular Paramagnetism* (Wiley, New York, 1976).

[7] P. Fulde, in *Strong Electron Correlations* (Springer, Berlin, 1992); C.-S. Neumann and P. Fulde, Z. Phys. B **74**, 277 (1989).

[8] J. G. Brennan, T. Siegrist, S. M. Stuczynski, and M. L. Steigerwald, J. Am. Chem. Soc. **111**, 9240 (1990).

[9] M. L. Steigerwald, T. Siegrist, and S. M. Stuczynski, Inorg. Chem. **30**, 2256 (1990).

[10] F. Jellinek, *MTP International Conference of Science, Inorganic Chemistry Series I* (Butterworths, London, 1972), Vol. 5, p. 339; J. Zaanen, G. Sawatsky, and P. Allen, Phys. Rev. Lett. **55**, 418 (1985).

[11] The situation for the CoTe clusters is less clear, CoTe being a magnetic small-gap semiconductor. One could argue that the triplet ground state in the doubly charged cluster is a manifestation of the greater tendency of these Co systems to become magnetic.

[12] R. A. Wheeler, J. Am. Chem. Soc. **112**, 8737 (1990).

[13] G. R. Steward, Rev. Mod. Phys. **56**, 755 (1984); P. A. Lee, T. M. Rice, J. W. Serence, L. J. Shaw, and J. W. Wilkins, Commun. Condens. Matter Phys. **12**, 99 (1986).

[14] G. Gruener and A. Sawadowski, Rep. Prog. Phys. **37**, 1497 (1974).

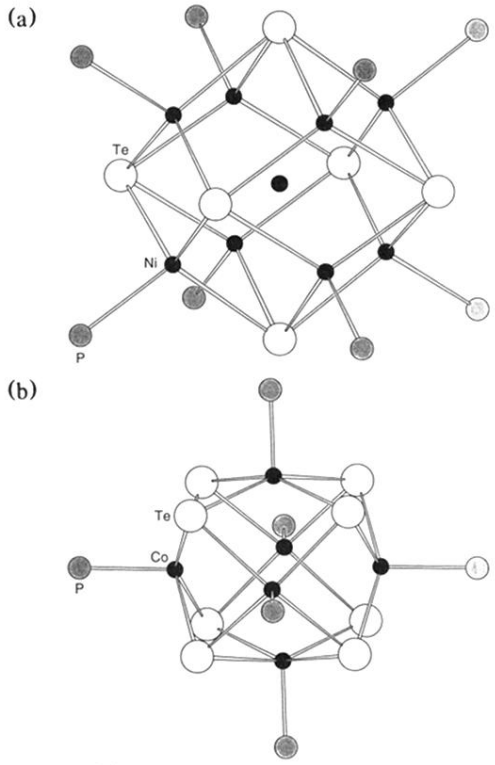

FIG. 1. (a) Crystallographically determined structure of $Ni_9Te_6(PEt_3)_8$. The large circles represent Te atoms, the small circles Ni atoms, and the intermediate-sized circles represent *P* atoms of the passivating ligands. The C and H atoms have been omitted for clarity. The average center-Ni surface-Ni distances are 2.47 Å. The average center-NiTe distance is 2.98 Å. The average surface-NiTe distance is 2.55 Å. Upon oxidation the cluster contracts slightly ($< 1\%$). Complete structural details are given in Ref. [8]. (b) Crystallographically determined structure of $Co_6Te_8(PEt_3)_6$. The large circles represent Te atoms, the small circles Co atoms, and the intermediate-sized circles represent *P* atoms of the passivating ligands. The C and H atoms have been omitted for clarity. The average Co-Te distance is 2.52 Å. The average Co-Co distance is 3.23 Å. Upon oxidation the cluster contracts slightly ($< 1\%$). Complete structural details are given in Ref. [9].